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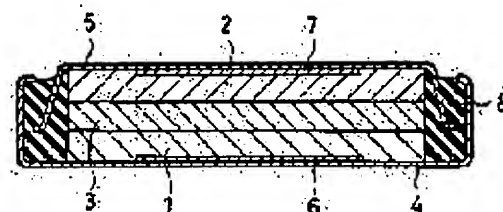
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(54) NON-AQUEOUS BATTERY

(57)Abstract:

PURPOSE: To provide a non-aqueous battery where an electric discharging capacity can be remarkably increased and thermal stability can be improved by reducing a change of crystal structure.

CONSTITUTION: In a non-aqueous battery provided with a negative electrode 2 and a positive electrode 1 each made of a material capable of storing and discharging lithium metal or lithium, an active material for the positive electrode 1 is $\text{Li}_a\text{MbNicCodOe}$ (wherein M represents at least one kind of metal selected from a group consisting of Al, Mn, Sn, In, Fe, V, Cu, Mg, Ti, Zn and Mo; $0 < a < 1.3$, $0.02 \leq b \leq 0.5$, $0.02 \leq d/c+d \leq 0.9$, $1.8 < e < 2.2$; and $b+c+d=1$).



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2. **** shows the word which can not be translated.
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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates especially to amelioration of a positive electrode about the nonaqueous rechargeable battery equipped with the negative electrode which uses lithium, lithium alloy, or lithium-carbon material, and the positive electrode.

[0002]

[Description of the Prior Art] As this kind of a rechargeable battery, an electrical potential difference is high and to be high capacity moreover is demanded. such a thing -- taking into consideration -- MoO_3 , V_2O_5 , a lithium-manganese system multiple oxide, MoS_2 , LiCoO_2 , or LiNiO_2 etc. -- positive active material is proposed and the part is put in practical use.

[0003] however, the above LiCoO_2 etc. -- when it used as positive active material, and the crystal structure changed a lot at the time of charge and discharge, the crystal structure was destroyed little by little and it had the technical problem that discharge capacity became small as a result.

[0004]

[Problem(s) to be Solved by the Invention] Then, LiCoO_2 LiNiO_2 Improved $\text{LiNix Co}_{1-x}\text{O}_2$ Although a cell which is used as positive active material is proposed, since the crystal structure changes too at the time of charge and discharge, discharge capacity becomes small. in addition, the above LiCoO_2 etc. -- it had the technical problem that thermal stability became low under existence of the electrolytic solution after charge.

[0005] This invention can be made in consideration of the starting actual condition, can reduce change of the crystal structure, can increase discharge capacity by leaps and bounds, and aims at offer of the nonaqueous cell which can moreover raise thermal stability.

[0006]

[Means for Solving the Problem] In the nonaqueous cell which has the negative electrode which consists of the ingredient which can occlusion emit a lithium metal or a lithium in order that this invention may attain the above-mentioned object, and a positive electrode as the active material of the above-mentioned positive electrode -- $\text{Li}_a\text{Mb Nic Cod Oe}$ (M -- aluminum --) It is a kind of metal chosen from the group which consists of Mn, Sn, In, Fe, V, Cu, Mg, Ti, Zn, and Mo at least. 0 [and] -- < -- the range of $a < 1.3$, $0.02 \leq b \leq 0.5$, $0.02 \leq d/c+d \leq 0.9$, and $1.8 < e < 2.2$ -- it is -- further -- $b+c+d=1$ -- it is -- it is characterized by using.

[0007] Moreover, said $\text{Li}_a\text{Mb Nic Cod Oe M}$ of the positive active material shown is characterized by being a kind of metal chosen from the group which consists of Cu and Fe at least.

[0008]

[Function] Like the above-mentioned configuration, it is $\text{Li}_a\text{Nic Cod Oe}$. If what added other metals M is used as positive active material, a reason is not certain, but even if Li is extracted at the time of charge, the crystal structure serves as stability comparatively. Therefore, charge and discharge are repeated, the crystal structure does not collapse as a line but reversible charge and discharge become possible.

[0009] Moreover, when M of positive active material is constituted from a kind of metal chosen from the group which consists of Cu and Fe at least, thermal stability can be raised by leaps and bounds under existence of the electrolytic solution after charge.

[0010]

[Example]

The [1st example] The 1st example of this invention is explained below based on drawing 1 - drawing 3.

[Example] Drawing 1 is the sectional view of the flat nonaqueous rechargeable battery concerning one example of this invention, and the negative electrode 2 which consists of a lithium is stuck to the inner surface of the negative-electrode charge collector 7 by pressure, and has fixed this negative-electrode charge collector 7 on the inner base of the negative-electrode can 5 which consists of ferritic stainless steel (SUS430). The peripheral

edge of the above-mentioned negative-electrode can 5 is being fixed to the interior of the insulating packing 8 made from polypropylene, and the positive-electrode can 4 which consists of stainless steel is being fixed to the periphery of the insulating packing 8. The positive-electrode charge collector 6 is being fixed to the inner base of this positive-electrode can 4, and it is $\text{LiMn}_{0.1}\text{Ni}_{0.45}\text{Co}_{0.45}\text{O}_2$ in the inner surface of this positive-electrode charge collector 6. The positive electrode 1 used as an active material is being fixed. Between this positive electrode 1 and said negative electrode 2, the separator 3 with which it consisted of the fine porosity film made from polypropylene, and impregnation of the electrolytic solution was carried out is inserted. What dissolved lithium perchlorate in volume mixed solvents, such as propylene carbonate and dimethoxyethane, at a rate of one mol/l. is used for the above-mentioned electrolytic solution. In addition, a cell dimension is 3.0mm in the diameter of 24.0mm, and thickness.

[0011] Here, the above-mentioned positive electrode 1 was produced as follows. first, Li_2CO_3 -- this mixture after mixing CO_3 (lithium carbonate), MnCO_3 (manganese carbonate), and NiCO_3 (nickel carbonate) and CoCO_3 (cobalt carbonate) with a mortar so that the mole ratio of Li, Mn, and nickel and Co may be set to 1:0.1:0.45:0.45 -- the inside of air -- 850 degrees C -- 20 hours -- heat-treating -- $\text{LiMn}_{0.1}\text{Ni}_{0.45}\text{Co}_{0.45}\text{O}_2$ from -- the positive active material which changes is produced. next, this positive-active-material powder, the acetylene black as an electric conduction agent, and the fluoro-resin powder as a binder -- a weight ratio -- the ratio of 90:6:4 -- mixing -- a positive electrode -- this positive electrode after producing a mixture -- a mixture -- 2 t/cm² Application-of-pressure molding was carried out at the diameter of 20mm, and it produced by heat-treating at 250 more degrees C.

[0012] On the other hand, the negative electrode 2 was produced by piercing a given thickness Mino lithium plate in diameter of 20mm. Thus, the produced cell is called the (A) cell below.

[Example of a comparison] MnCO_3 It is Li_2CO_3 so that it may not add and the mole ratio of Li, and nickel and Co may be set to 1:0.5:0.5. NiCO_3 CoCO_3 It mixed and also the cell was produced like the above-mentioned example.

[0013] Thus, the produced cell is called the (X) cell below.

[Experiment 1] Since the discharge capacity in the (A) cell of this invention and the (X) cell of the example of a comparison was investigated, the result is shown in a table 1. In addition, charge-and-discharge conditions are conditions of discharging to discharge-final-voltage 3.0V by 3mA of discharge currents, after charging to charge termination electrical-potential-difference 4.3V by 1mA of charging currents.

[0014]

[A table 1]

電池	放電容量 (mAh)
A	1 7 0
X	1 5 9

[0015] As for the (A) cell of this invention, it is admitted that discharge capacity is increasing compared with the (X) cell of the example of a comparison so that more clearly than the above-mentioned table 1.

[experiment 2] -- the cell to which the value of d/c+d of $\text{Li}_{1.0}\text{Ni}_x\text{Co}_{0.2}\text{O}_2$ (positive active material) was changed -- [-- that is the above -- a comparison -- an example -- (-- X --) -- a cell -- resemblance -- a cell --] -- and -- $\text{Li}_{1.0}\text{Mn}_{0.1}\text{Ni}_x\text{Co}_{0.2}\text{O}_2$ (positive active material) -- d -- the cell to which the value of 'c'+d' was changed -- [-- that is the above -- this invention -- (-- A --) -- a cell -- resemblance -- a cell -- it is -- c -- ' -- = -- 0.9 -- x -- c -- d -- ' -- = -- 0.9 -- x -- d -- expressing -- having --] -- it can set -- discharge -- capacity -- having investigated -- since -- the result -- drawing 2 -- being shown . In addition, experiment conditions are the same conditions as the above-mentioned experiment 1.

[0016] Even if it is the case where c (c') and d (d') are which values so that clearly from drawing 2 , it is admitted that discharge capacity is large from the cell by which the direction of the cell which added Mn does not add Mn. It is admitted that discharge capacity is [the value of d/c+d] large between 0.02-0.9 especially.

[Experiment 3] Since discharge capacity at the time of changing the addition of Mn (x being changed in $\text{Li}_{1.0}\text{Mn}_x\text{Ni}_{0.5-x/2}\text{Co}_{0.5-x/2}\text{O}_2$) was measured, the result is shown in drawing 3 . In addition, experiment conditions are the same conditions as the above-mentioned experiment 1.

[0017] It is admitted that discharge capacity is [the rate which Mn adds] large by the mole ratio from 0.02 to 0.5 (namely, $\text{Li}_{1.0}\text{Mn}_x\text{Ni}_{0.5-x/2}\text{Co}_{0.5-x/2}\text{O}_2$ the range of $0.02 \leq x \leq 0.5$), and it is admitted that discharge capacity is increasing by leaps and bounds from 0.02 to 0.2 especially so that clearly from drawing 3 .

[0018] Therefore, it is a mole ratio, the rate which Mn adds needs to be from 0.02 to 0.5, and it is especially

desirable that it is from 0.02 to 0.2.

[The 2nd example]

a [example] -- Li_2CO_3 CuO and NiCO_3 CoCO_3 this mixture after mixing with a mortar so that the mole ratio of Li, Cu, and nickel and Co may be set to 1:0.1:0.45:0.45 -- the inside of air -- 850 degrees C -- 20 hours -- heat-treating -- $\text{Li}_{1.0}\text{Mn}_{0.1}\text{nickel}_{0.45}\text{Co}_{0.45}\text{O}_{2.0}$ from -- the positive active material which changes is produced. And this positive active material was used, and also the cell was produced like the example of said 1st example.

[0019] Thus, the produced cell is called the (B) cell below.

[Experiment 1] Since the discharge capacity in the (B) cell of above-mentioned this invention and the (X) cell of the example of a comparison shown in said 1st example was investigated, the result is shown in a table 2. In addition, charge-and-discharge conditions are the same conditions as the experiment 1 of said 1st example.

[0020]

[A table 2]

電池	放電容量 (mAh)
B	1 7 3
X	1 5 9

[0021] As for the (B) cell of this invention, it is admitted that discharge capacity is increasing compared with the (X) cell of the example of a comparison so that more clearly than the above-mentioned table 2.

[experiment 2] -- the cell to which the value of $d/c+d$ of $\text{Li}_{1.0}\text{NiCoO}_{2.0}$ (positive active material) was changed -- [-- that is the above -- a comparison -- an example -- (-- X --) -- a cell -- resemblance -- a cell --] -- and -- Li -- 1.0 -- Cu -- 0.1 -- $\text{NiCoO}_{2.0}$ (positive active material) -- d -- the cell to which the value of $'c'+d'$ was changed -- [-- that is the above -- this invention -- (-- B --) -- a cell -- resemblance -- a cell -- it is -- c -- ' -- == -- 0.9 -- x -- c -- d -- ' -- == -- 0.9 -- x -- d -- expressing -- having --] -- it can set -- discharge -- capacity -- having investigated -- since -- the result -- drawing 4 -- being shown . In addition, experiment conditions are the same conditions as the experiment 1 of said 1st example.

[0022] Even if it is the case where c (c') and d (d') are which values so that clearly from drawing 4 , it is admitted that discharge capacity is large from the cell by which the direction of the cell which added Cu does not add Cu. It is admitted that discharge capacity is [the value of $d/c+d$] large between 0.02-0.9 especially.

[Experiment 3] Since discharge capacity at the time of changing the addition of Cu (x being changed in $\text{Li}_{1.0}\text{Cu}_x\text{nickel}_{0.5-x/2}\text{Co}_{0.5-x/2}\text{O}_{2.0}$) was measured, the result is shown in drawing 5 . In addition, experiment conditions are the same conditions as the experiment 1 of said 1st example.

[0023] It is admitted that discharge capacity is [the rate which Cu adds] large by the mole ratio from 0.02 to 0.5 (namely, $\text{Li}_{1.0}\text{Cu}_x\text{nickel}_{0.5-x/2}\text{Co}_{0.5-x/2}\text{O}_{2.0}$ the range of $0.02 \leq x \leq 0.5$), and it is admitted that discharge capacity is increasing by leaps and bounds from 0.02 to 0.2 especially so that clearly from drawing 5 .

[0024] Therefore, it is a mole ratio, the rate which Cu adds needs to be from 0.02 to 0.5, and it is especially desirable that it is from 0.02 to 0.2.

[The 3rd example]

a [example] -- Li_2CO_3 FeOOH and NiCO_3 CoCO_3 this mixture after mixing with a mortar so that the mole ratio of Li, Fe, and nickel and Co may be set to 1:0.1:0.45:0.45 -- the inside of air -- 850 degrees C -- 20 hours -- heat-treating -- $\text{Li}_{1.0}\text{Fe}_{0.1}\text{nickel}_{0.45}\text{Co}_{0.45}\text{O}_{2.0}$ from -- the positive active material which changes is produced. And this positive active material was used, and also the cell was produced like the example of said 1st example.

[0025] Thus, the produced cell is called the (C) cell below.

[Experiment 1] Since the discharge capacity in the (C) cell of above-mentioned this invention and the (X) cell of the example of a comparison shown in said 1st example was investigated, the result is shown in a table 3. In addition, charge-and-discharge conditions are the same conditions as the experiment 1 of said 1st example.

[0026]

[A table 3]

電池	放電容量 (mAh)
C	1 7 5
X	1 5 9

[0027] As for the (C) cell of this invention, it is admitted that discharge capacity is increasing compared with the (X) cell of the example of a comparison so that more clearly than the above-mentioned table 3.

[experiment 2] -- the cell to which the value of $d/c+d$ of Li1.0 Nic Cod O2.0 (positive active material) was changed -- [-- that is the above -- a comparison -- an example -- (-- X --) -- a cell -- resemblance -- a cell --] -- and -- Li -- 1.0 -- Fe -- 0.1 -- Nic'Cod'O -- 2.0 (positive active material) -- d -- the cell to which the value of $'/c'+d$ was changed -- [-- that is the above -- this invention -- (-- C --) -- a cell -- resemblance -- a cell -- it is -- c -- ' -- = -- 0.9 -- x -- c -- d -- ' -- = -- 0.9 -- x -- d -- expressing -- having --] -- it can set -- discharge -- capacity -- having investigated -- since -- the result -- drawing 6 -- being shown . In addition, experiment conditions are the same conditions as the experiment 1 of said 1st example.

[0028] Even if it is the case where c (c') and d (d') are which values so that clearly from drawing 6 , it is admitted that discharge capacity is large from the cell by which the direction of the cell which added Fe does not add Fe. It is admitted that discharge capacity is [the value of $d/c+d$] large between 0.02-0.9 especially.

[Experiment 3] Since discharge capacity at the time of changing the addition of Fe (x being changed in Li1.0 Fex nickel0.5-x/2 Co0.5-x/2 O2.0) was measured, the result is shown in drawing 7 . In addition, experiment conditions are the same conditions as the experiment 1 of said 1st example.

[0029] It is admitted that discharge capacity is [the rate which Fe adds] large by the mole ratio from 0.02 to 0.5 (namely, Li1.0 Fex nickel0.5-x/2 Co0.5- x/the presentation of 2O2.0 the range of $0.02 \leq x \leq 0.5$), and it is admitted that discharge capacity is increasing by leaps and bounds from 0.02 to 0.2 especially so that clearly from drawing 7 .

[0030] Therefore, it is a mole ratio, the rate which Fe adds needs to be from 0.02 to 0.5, and it is especially desirable that it is from 0.02 to 0.2. Moreover, also when aluminum, Sn, In, V, Mg, Ti, Zn, and Mo are added as an addition metal, it is checking having the same effectiveness as the above by experiment. And also in these cases, an addition rate needs to be from 0.02 to 0.5 like the above-mentioned experiment 3, and it is checking especially that it is also desirable that it is from 0.02 to 0.2.

[Experiment 4] Li1.0 M0.1 Nic Cod O2.0 (as M) Fe, Cu, Mn, aluminum, Sn, In, V, Mg, Ti, Zn, and Mo -- an activity and Li1.0 Nic Cod O2.0 from, in order to investigate the thermal stability of the positive active material (however, $d/c+d$ change) which changes The positive electrode using such positive active material is charged, this positive electrode and electrolytic solution that were charged are heated, and since the temperature which produces exothermic reaction was measured by thermal analysis, that result is shown in drawing 8 .

[0031] The positive active material (Li1.0 M0.1Nic Cod O2.0) used for the cell of this invention is excellent in stability more nearly thermal than the positive active material (Li1.0 Nic Cod O2.0) used for the cell of the example of a comparison, and it is admitted in the positive active material using Cu or Fe especially as M that thermal stability is improving by leaps and bounds so that clearly from drawing 8 .

[Other matters]

** In the above-mentioned example, although a lithium carbonate and cobalt carbonate were respectively used as a lithium compound and a cobalt compound, it is possible not to limit to these and to use oxides of others, such as a lithium hydroxide, lithium oxide, a lithium nitrate, a phosphoric-acid lithium, a cobalt nitrate, cobalt carbonate, or oxalic acid cobalt, a carbonate, and a hydroxide. Moreover, the same is said of a nickel compound and other addition metals.

** Don't limit this invention to the rechargeable battery using the nonaqueous electrolyte shown in the example, it can apply also to the nonaqueous rechargeable battery using a solid electrolyte, and things are natural. Moreover, it is possible to apply also to the nonaqueous primary cell using nonaqueous electrolyte or a solid electrolyte.

** At the above-mentioned example, it is Lia Mb Nic Cod Oe. Although it sets and is referred to as $a=1.0$, if it is $0 < a < 1.3$, it will check having the same effectiveness as the above by experiment. Moreover, although referred to as $e=2$, if it is $1.8 < e < 2.2$, it will check having the same effectiveness as the above by experiment.

** At the above-mentioned example, it is Li1.0 M0.1 nickel0.45Co 0.45O2.0. Although heat treatment temperature at the time of creating is made into 850 degrees C, if it is 500-1000 degrees C, it is Li1.0 M0.1 nickel0.45Co 0.45O2.0 of the same configuration. It is checking by experiment that it can create.

[0032]

[Effect of the Invention] Since the discharge capacity of a nonaqueous primary cell and a nonaqueous

rechargeable battery can be raised since the crystal structure is stabilized according to this invention as explained above, and charge and discharge are repeated and the crystal structure does not collapse as a line, the outstanding effectiveness that the cycle property of a nonaqueous rechargeable battery can be raised is done so.

[Translation done.]